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[12] Utility Model Patent Descriptions

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Utility Model Name: An Organic Thin Film Electroluminescent Device

Abstract

The utility model relates to an organic thin film electroluminescent (EL) device, particularly to a high efficient and transparent organic thin film electroluminescent device having a driving voltage of less than about 4V, of which the cathode is constituted by a transparent electron excitation electrode, as makes that the device can emit light directly from the cathode surface. The constitution of the device includes sequentially a hole excitation electrode, a hole transport layer, a light emitting layer, ~~a metal salt-doped layer and/or a metal-doped layer~~, and a transparent electron excitation electrode. The hole excitation electrode of the device can be constructed on a Si wafer integrated circuit, so as to highly simplify the driving thereof. Moreover, the device does not need moulding at the cathode so as to highly simplify the production process and significantly reduce the cost. The organic thin film EL device is suitable for various panel displays including monochromatic and color displays which are new generation EL products with a strong commercial competitiveness.

Claims:

1. A transparent organic thin film electroluminescent device, characterized in that: a metal-doped layer and/or a metal salt-doped layer exist(s) as an electron transport layer between a transparent electron excitation electrode, i.e. cathode, and a light emitting layer.
2. The transparent organic thin film electroluminescent device according to claim 1, the structure thereof comprises sequentially the following: a substrate, a hole excitation electrode, a hole transport layer, a light emitting layer, a metal salt-doped layer and/or a metal-doped layer and a transparent electron excitation electrode.

3. The transparent organic thin film electroluminescent device according to claim 1, wherein the doped metals include alkaline metals, alkaline earth metals, transition metals and rare earth metals with a work function of less than or equal to 4.2eV; the doped metal salts include alkaline metal salts, alkaline earth metal salts, transition metal salts and rare earth metal salts with a work function of less than or equal to 4.2eV.

4. The transparent organic thin film electroluminescent device according to claim 3, wherein the metal salt-doped layer has a doping concentration of metal salts of 0.1-100% by weight, and the metal-doped layer has a doping concentration of metals of 0.1-99% by weight.

5. The transparent organic thin film electroluminescent device according to claim 4, wherein the metal salt-doped layer has a thickness of 1-3000Å and the metal-doped layer has a thickness of 10-3000Å.

6. The transparent organic thin film electroluminescent device according to claim 3, wherein the doped metals are selected from the group consisting of Li, Na, K, Be, Mg, Ca, Sr, Ba, Y, La, Sm, Gd and Yb.

7. The transparent organic thin film electroluminescent device according to claim 3, wherein the doped metal salts are selected from the group consisting of fluorides, oxides, chlorides, iodides and tellurides of alkaline metals and alkaline earth metals.

8. The transparent organic thin film electroluminescent device according to claim 7, wherein the doped metal salts are selected from the group consisting of LiF, NaF, KF, RbF, CsF, MgF₂, CaF₂, SrF₂, BaF₂, Li₂O, Na₂O, K₂O, Rb₂O, Cs₂O, MgO, CaO, SrO, BaO, LiI, NaI and KI.

9. The transparent organic thin film electroluminescent device according to claim 6 or 8, wherein the material of the transparent electron excitation electrode may be selected from the group consisting of indium-tin oxide(ITO), Au, SnO₂, conductive polymers and ZnO₂.

10. The transparent organic thin film electroluminescent device according to claim 9, wherein the hole excitation electrode is prepared by a sputtering deposition process.

11. The transparent organic thin film electroluminescent device according to claim 1, wherein the hole excitation electrode is constructed on a Si wafer integrated circuit.

12. The transparent organic thin film electroluminescent device according to claim 6 or 8, wherein the organic materials of the metal salt-doped layer and the metal-doped layer are organic compounds of heteroatoms which contain lone electron pairs, wherein the heteroatoms are selected from the group consisting of N, O, S and P.

13. The transparent organic thin film electroluminescent device according to claim 12, wherein the organic compounds of heteroatoms which contain lone electron pairs are transparent and have a maximum absorption spectrum at wavelengths less than 450nm.

14. The transparent organic thin film electroluminescent device according to claims 2-8 and 13, wherein the materials of the hole transport layer and the light emitting layer are organic macromolecular polymers.

15. The transparent organic thin film electroluminescent device according to claim 14, wherein the metals and metal salts doped respectively in the metal-doped layer and the metal salt-doped layer are of a discontinuous distribution.

Description

This utility model relates to an organic thin film electroluminescent (EL) device, and more particularly, to a multi-layered organic thin film EL device which is low voltage driven and emits light from the cathode surface. In the multi-layered organic thin film EL device herein, the electron transport layer is constituted by an organic material doped with metals and/or metal compounds, resulting the decrease of the driving voltage; the cathode thereof is constituted by a transparent electron excitation electrode and thus the device can emit light directly from the surface of cathode. The organic thin film EL device of this utility model

is applicable to various panel display including monochromatic and color displays.

As information era develops rapidly, particularly, the popularization and utilization of computers, color displays, especially ultra-thin, high-resolution color panel displays attract much attention. Of the portable panel display having a high efficiency, liquid crystal display (LCD) has been commercialized. However, the liquid crystal display has the following disadvantages of narrow viewing angle, slow response, not self-luminescing, great energy consumption for the background light when placed at dark circumstances and high production cost.

Light emitting diode (LED)-like type of display is the next generation product. LED is an active luminescing technology and no viewing angle difference exists. However, owing to the inorganic materials employed and the limit of processing technique, the LED display also needs a high production cost and a driving voltage of up to hundreds of voltage.

Organic EL panel display is recently developed and has a greatly potential market competitiveness. It has overall advantages with respect to production process, light luminance and efficiency, driving voltage, resolution, multi-coloration, response time and the like. Moreover, it has a high response velocity and no problems relating to viewing angle, so it invokes much concern.

Organic EL technique has been present for more than 30 years. But, the organic EL devices has a vital defect, i.e. driving voltage thereof being over 200V, which limits its application.

As early as in 1965, Gurnee *et al* disclosed firstly the patent relating to organic EL devices (US3172862; 3173050). Dresner also published a patent regarding organic EL device in 1973 (US3170167). In these patents, polyaromatic-ring organic compounds such as anthracene, naphthacene, pentacene and the like were used as organic EL materials. These early organic EL devices have main structural characteristics of single layer, wherein the organic light-emitting layer has a thickness of

over 1mm and the driving voltage is over 200V.

In the 1980s, Kodak Company, US, disclosed firstly a ultra-thin multi-layered organic EL device structure which highly decreased the driving voltage of the device. The device has the following basic characteristics of employing conductive glass as a substrate, and a hole injection layer (100nm, which also acts as the conductive layer) being coated by vaporization, an electron transport layer which also acts as the light-emitting layer being spin coated, and then a metal layer being plated as the negative electrode; the device having a driving voltage of 20V and a luminance of 5 cd/m². Later, Kodak Company used aromatic polyamines as the hole transporting material, as highly improves the device performance and makes the luminance up to 340 cd/m².

Thereafter, a series of EL materials were developed. It is to be noted that, in the last ten years, owing to the continuous development of materials and device processing techniques, organic EL technique has approached to or come to the practical application phase.

Nowadays, the organic EL devices are generally of a multi-layered composite structure including a transparent indium-tin oxide (ITO) anode, a hole transport layer, a light-emitting layer, an electron transport layer and an opaque metal cathode (Al, Mg/Ag alloy or Al/Li alloy). The hole transport layer is used to transport the holes injected by the anode to the light-emitting layer, while the electron transport layer transports the electrons injected by the cathode to the light-emitting layer. When the hole transport layer is interposed between the light-emitting layer and the anode, more holes are injected into the light-emitting layer under a low electric field and encountered the electrons in the light-emitting layer injected from the electron transport layer to form excitons, leading to luminescence ultimately. However, the current organic EL devices mostly have a driving voltage of 10V to maintain a normal luminance, a great energy consumption and a complex driving system. Moreover, the processing technique therein is quite complex since the moulding at the cathode is required, and the requirement on the preparation process is also

demanding.

The difficulty for the current organic EL device to further reduce the driving voltage thereof arises from an energy level difference between the cathode and the light-emitting layer, which makes the carrier difficult to be injected from the cathode into the light-emitting layer containing organic dye molecules. As a result, improving the injection of carries has been considered as one of the key factors for improving the organic EL devices. In order to lower the work function of the cathode and the potential energy barrier of electron injection to make it equivalent to the LUMO (Lowest Unoccupied Molecular Orbital) of the electron transport layer, more studies have been carried out. Mg/Ag or Al/Li alloy has been known as one of the most ideal cathode materials for this purpose. But the metals having a low work function is of a poor environmental stability, and is extremely sensitive to a damp environment, as makes the fabrication process complex and cost increased. Furthermore, the metals will be eroded when being exposed to air. So, the device should be encapsulated.

Moreover, the general organic EL devices are constructed on a transparent substrate such as a glass substrate, through which the light emitted by the devices passes. Because the upper layer of the devices, i.e. cathode, is opaque, the light can but irradiate out through the hole excitation electrode, resulting in the producing process complex. Especially, in the case that Si wafer is chosen as the substrate, the light emitted by the device are blocked, as exerts limit on the selection of device materials. Therefore, there is a need that the electron excitation electrode would be prepared to be transmissive so that the light emitted by the organic EL device can pass through this electrode layer to display. This structure is generally called as "surface-irradiating organic electroluminescent (EL) device".

Many attempts has been done to decrease the energy level difference between the electron transport layer and the light emitting layer by selection of the materials of electron transport layer, but the existing

organic electron transport materials can not fulfill the following requirements simultaneously of 1) good electron-conducting property; 2) excellent moulding property; 3) good stability to light, electricity and heat during the production process and 4) transparency.

The purpose of this utility model is to overcome the problems of the existing organic EL devices and provide a high efficient and stable organic EL device which employs no active metal as the cathode.

Another purpose of this utility model is to provide an organic EL device in which the anode is constructed on an opaque Si wafer integrated circuit.

More particularly, the purpose of this utility model is to provide an organic thin film EL device having a novel structure and being high emission transparent and easy to drive and having a driving voltage being half that of the current devices.

Another purpose of this utility model is to provide a high efficient organic EL display device having a transparent electron excitation layer. The electron excitation layer consists of transparent electron excitation electrodes. Thus, the EL display may display from the surface of electron excitation electrodes, as modifies the complex production process of the existing organic EL display arising from the display only from the hole excitation electrode.

Another purpose of this utility model is to decrease the energy level difference by which the electron excitation electrode motivates the electrons to the light-emitting layer. ~~An electron transport layer doped with metals and/or metal salts is added between the electron excitation electrode and the light emitting layer to reduce the driving voltage.~~

This utility model utilizes as an electron-rich dopant the metals or metal salts doped in the transparent electron-transport organic compounds. No matter what kind of electron excitation electrode is employed, the energy level difference between the electrode and the organic compound layer can be eliminated so as to decrease the driving voltage.

In order to achieve said purposes, this utility model designs an organic EL device with a multi-layered composite structure, wherein a metal-doped layer and a metal salt-doped layer are added as the electron transport layer between the transparent electron excitation electrode, i.e. cathode, and the light-emitting layer. The device includes sequentially a substrate, a hole excitation electrode, a hole transport layer, a light emitting layer, a metal-doped layer and/or a metal salt-doped layer and a transparent electron excitation electrode.

The hole excitation electrode of the organic EL device according to this utility model can be constructed on a Si wafer integrated circuit and a transparent glass substrate.

This utility model will be detailedly described as follows in combination with the drawings.

Fig.1 shows the schematic structure of the organic EL display device according to this utility model.

This utility model provides an organic EL device with a multi-layered composite structure, wherein the structural constitution thereof is characterized in: (1) the device substrate, (2) the hole excitation electrode, e.g. Indium-Tin-Oxide (ITO) electrode, (3) the hole transport layer, (4) the light emitting layer, (5) the metal salt-doped electron transport layer, (6) the metal-doped electron transport layer and (7) the transparent electron excitation electrode which may be a transparent ITO electrode.

In addition to the laminate structure mentioned above, the organic EL device according to this utility model may also include other laminate structures, such as hole excitation electrode/hole transport layer/light emitting layer/metal salt-doped electron transport layer/transparent electron excitation electrode, and hole excitation electrode/hole transport layer/light emitting layer/metal-doped electron transport layer/transparent electron excitation electrode. It is to be noted that this utility model can be of any laminate structure, provided a metal- or metal salt-doped electron transport layer and a transparent electron excitation electrode are

included.

Regarding the organic EL display according to this utility model, electrons and holes are excited and injected from the cathode and anode separately, transported in the hole transport layer and the electron transport layer respectively, and then combined in the area around the interface between the two layers to generate excitons. The excitons transit to the ground state by irradiation and thus emit light. The excitation of electrons from the cathode to the dielectric organic compound layer is based on the reduction of the organic compounds in the electron transport layer on the surface of the cathode, so as to generate the free anion state. In this utility model, the doped metals or metal salts are pre-doped into the electron transport organic compound layer in contact the cathode, and serve the function of reducing the organic compounds. As a result, the energy level difference generated during the excitation and injection of electrons from the cathode is reduced. Because the metal- or metal salt-doped layer comprises the reduced molecules (*i.e.* molecules which have accepted electrons and contain electrons) and have a less energy level for the injected electron, the driving voltage is reduced.

The substrate used in the device according to this invention is a single crystal semiconductor substrate selected from the group consisting of Si, Ge, GaAs, GaP, GaN, GaSb, InAs, InP, InSb or $\text{Al}_x\text{Ga}_{1-x}\text{As}$, wherein x is 0-1. The substrate may be undoped, slightly doped or much doped, and may be bare or covered with a layer of dielectric material, such as silica or silicon nitride. In the practical use, a part of semiconductor material can be made as the substrate of the device, and other semiconductor wafers can be processed into a driver, switches or other circuits.

In the device structures of this utility model, the metal doped in the metal-doped electron transport layer (6) is not limited to any particular one, given it can reduce the organic compounds. It includes alkali metal such as Li, alkali earth metal such as Mg, transition metals comprising rare earth metals, which has a work function less than or equal to 4.2eV. The typical examples of the doped metal includes Li, Na, K, Be, Mg, Ca,

Sr, Ba, Y, La, Sm, Gd, Yb. The metals has a doping concentration of 0.1-99% by weight and a thickness of 10-3000Å.

The metal salt doped in the metal salt-doped electron transport layer (5) comprises alkali metal salt, alkali earth metal salt, transition metal salt and rare earth metal salt, and has a work function less than or equal to 4.2eV. The metal salt doped in the organic EL devices according to this utility model must have a low electron-absorbing property or a strong dipolarity, as is the key feature of the material possibly selected. In addition to the fluorides and oxides of alkaline metals and alkaline earth metals, other seletable materials include mixture, chlorides, iodides and tellurides thereof. The particular examples include LiF, NaF, KF, RbF, CsF, MgF₂, CaF₂, SrF₂, BaF₂, Li₂O, Na₂O, K₂O, Rb₂O, Cs₂O, MgO, CaO, SrO, BaO, LiI, NaI, KI and the like. The metal salts have a doping concentration of 0.1-100% by weight and may be 1-3000Å thick.

If the doping concentration of the metals is lower than 0.1%, then the doping effect is less because the concentration of the reduced organic compounds is significantly decreased. If the doping concentration overpasses 99%, then the doping effect will also be reduced because the concentration of the doped electrons in the electron transport layer is obviously higher than that of the organic compound molecules and thus the concentration of the reduced molecules greatly reduces. Also, the thickness of the metal-doped layer had better be not less than 10Å, otherwise only a small amount of the reduced molecules are distributed on the interface surface of the electrodes, giving a weak doping effect. Similarly, the thickness had better be not higher than 3000Å, because this will lead to an excessive increase of the gross thickness of the electron transport layer, so as to increase the driving voltage.

Any moulding processes can be used to prepare the metal-doped layer and metal salt-doped layer in this utility model. The typical processes include vapor deposition process and sputtering process. And the spin-coating process and dipping coating process can also be used.

With respect to the material of the transparent electron excitation

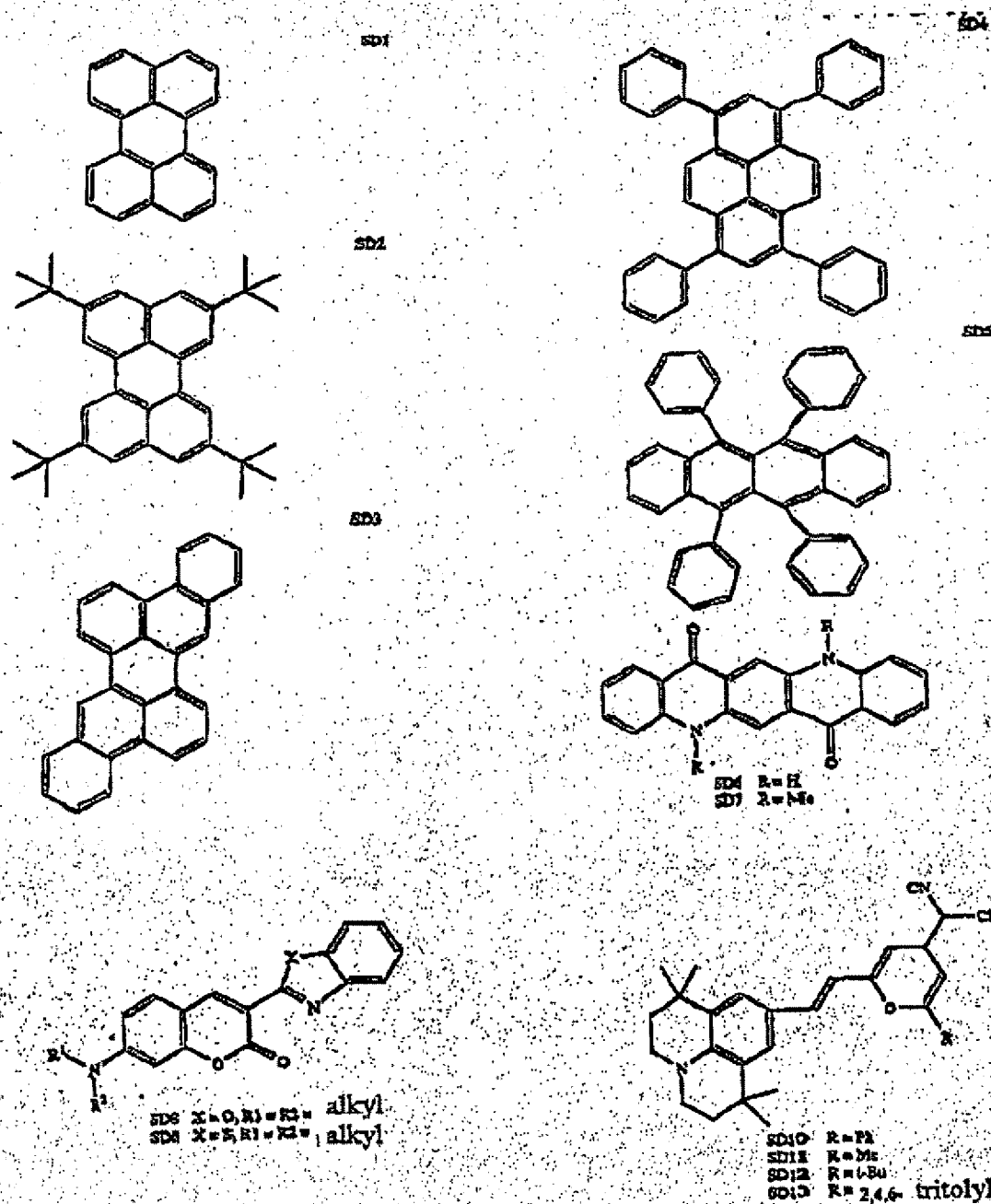
electrode according to this utility model, indium-tin oxide (ITO), Au, SnO₂, conductive polymer and ZnO₂ can be used. The hole excitation electrode can be made into a conventionally transparent or opaque electrode.

The material of the hole transport layer is one comprising the holes capable of accepting the anode and transporting them. It is not limit to any type and can be any hole transport material well known in the art, including, but not limited to, aromatic amines compounds disclosed in JP-A-6-25659, 6-203963, 6-215874, 7-145116, 7-224012, 7-157473, 8-48656, 7-126226, 7-188130, 8-40996, 8-40997, 7-126225, 7-1011911 and 7-97355, the particular examples thereof including

N,N,N',N'-tetraphenyl-4,4'-diaminobiphenyl,
 N,N'-diphenyl-N,N'-bis(3-methylphenyl)-4,4'-diaminobiphenyl,
 2,2-bis(4-di-p-tolylaminophenyl)propane,
 N,N,N',N'-tetra-p-tolul-4,4'-diaminobiphenyl,
 bis(4-di-p-tolylaminophenyl)phenylmethane,
 N,N'-diphenyl-N,N'-bis(4-methoxyphenyl)-4,4'-diaminobiphenyl,
 N,N,N',N'-tetraphenyl-4,4'-diaminodiphenylether,
 4-N,N-diphenylamino-(2-diphenylvinyl)benzene,
 1,1-bis(4-di-p-triaminophenyl)cyclohexane,
 1,1-bis(4-di-p-triaminophenyl)-4-phenylcyclohexane,
 bis(4-di-methylamino-2-methylphenyl)phenylmethane,
 N,N,N-tri(p-tolyl)amine,
 4-(di-p-tolylamino)-4'-[4-(di-p-tolyl)amino]styryl]stilbene,
 N,N,N',N'-tetraphenyl-4,4'-diaminobiphenyl, N-phenylcarbazole;
 4,4'-bis[N-(1-naphthyl)-N-phenylamino]-p-terphenyl,
 4,4'-bis[N-(2-naphthyl)-N-phenylamino]biphenyl,
 4,4'-bis[N-(3-acetylnaphthalenemethylidyne)-N-phenylamino]naphthalen
 e, 4,4'-bis[N-(9-anthryl)-N-phenylamino]biphenyl,
 4,4'-bis[N-(1-anthryl)-N-phenylamino]-p-terphenyl,
 4,4'-bis[N-(2-phenanthryl)-N-phenylamino]biphenyl,
 4,4'-bis[N-(8-fluoranthryl)-N-phenylamino]biphenyl,

4,4'-bis[N-(2-pyrenyl)-N-phenylamino]biphenyl,
 4,4'-bis[N-(1-coronyl)-N-phenylamino]biphenyl,
 2,6-bis(di-p-tolylamino)naphthalene,
 2,6-bis[di(1-naphthyl)amino]naphthalene,
 2,6-bis[N-(1-naphthyl)-N-(2-naphthyl)amino]naphthalene,
 4,4''-bis[N,N-di(2-naphthyl)amino]terphenyl,
 4,4''-bis[N-phenyl-N-[4-(1-naphthyl)phenyl]amino]biphenyl,
 4,4'-bis[N-phenyl-N-(2-pyrenyl)amino]biphenyl,
 2,6-bis[N,N-di(2-naphthyl)amino]fluorene,
 4,4'-(N,N-di-p-tolylamino)terphenyl, and
 di(N-1-naphthyl)(N-2-naphthyl)amine. The hole transport layer has a
 thickness of 300-5000Å.

The material used in the light emitting layer may be any organic light-emitting material used in the organic EL devices well know in the art. It may be the organic material having a high fluorescence or phosphorescence efficiency when used in a film state, such as ALQ. It may also be the hybrid light-emitting material prepared by doping a guest material with these organic materials having high fluorescence or phosphorescence efficiency, wherein said guest material includes, but not limited to, the compounds having the following general formulae:



The light-emitting layer is 50-5000Å thick.

The organic materials used in the metal- and metal salt-doped layer of the organic EL devices according to this utility model are not limited to any particular one. They are the organic compounds of heteroatoms which contain lone electron pairs, wherein the heteroatoms are N, O, S and P. Said organic compounds of heteroatoms containing lone electron pairs are transparent and have a maximum absorption spectrum at a

wavelength less than 450nm. Suitable examples of the organic compounds include polycyclic compounds such as terphenyl, quaterphenyl and derivatives thereof, condensed polycyclic hydrocarbon compounds such as naphthalene, tetracene, pyrene, coronene, anthracene, diphenyl anthracene, phenanthrene and derivatives thereof, condensed heterocyclic compounds such as phenanthroline, bathophenanthroline, phenanthridine, acridine, quinoline, quinoxaline, phenazine and the like and derivatives thereof, and diphenyl butadiene, tetraphenyl butadiene, oxadiazole, aldazine, dibenzoxaline, distyrene, pyrazine, cyclopentadiene, 8-hydroxyquinoline, aminoquinoline, imine, diphenyl ethylene, vinyl anthracene, diaminocarbazole, pyrane, thiopyrane, polymethine, merocyanine, quinacridine, rubrene and derivatives thereof. In addition to the aforesaid organic compounds, the metal chelated compounds disclosed in JP-A-63-295695, 8-22557, 8-81472, 5-9470 and 5-17764 are also suitable. On these metal chelated compounds, suitable are the metal chelates which employs 8-hydroxyquinoline and derivatives thereof as ligands. The specific examples of ligands are tri(8-hydroxyquinoline) aluminum, di(8-hydroxyquinoline) magnesium, di[benzo-8-hydroxyquinoline] zinc, di(2-methyl-8-hydroxyquinoline) aluminum, tri(8-hydroxyquinoline) indium, tri(5-methyl-8-hydroxyquinoline) aluminum, 8-hydroxyquinoline lithium, tri(5-chloro-8-hydroxyquinoline) gallium, di(5-chloro-8-hydroxyquinoline) calcium. Other suitable materials are diarylbutadiene and stilbene such as those disclosed in US4356429, the materials used as the fluorescence whitening agents disclosed in US4539507, and the fluorescence whitening agents listed in *Synthetic Dye Chemistry*, pp.618-637, vol.5, 1971. 2,5-bis(5,7-di-t-pentyl-2-benzoxazolyl)-1,3,4-thiazole is especially suitable.

The process for preparing the organic EL devices according to this utility model is described below:

- (1) choosing one strip of ITO transparent conductive glass electrode

which has been photoetched into a strip electrode, wherein the line density is 3-4/mm.

(2) vacuum coating by vaporization a hole transport material having hole transporting properties on the ITO transparent conductive glass electrode;

(3) coating by vaporization a layer of light-emitting material on the hole transport layer to form a light emitting layer;

(4) after the formation of the light emitting layer, under a controlled vacuum, evaporating simultaneously ~~a material of electron transport layer together with metals and metal salts on the light emitting layer~~ to make the doped metals or metal salts reach the concentration range of this utility model, thus forming a metal-doped layer and/or a metal salt-doped layer with a total thickness of 1-3000Å; and

(5) depositing an ITO layer on the metal-doped layer and/or metal salt-doped layer by a sputtering system, to get a thickness of 50-5000Å.

The organic EL devices according to this utility model will be further illustrated with examples.

A strip of ITO transparent conductive glass electrode is chosen, wherein said glass electrode has been photoetched into a strip electrode and has a line density of 3-4/mm; on the glass substrate plated with ITO, a TPD hole transport layer having a thickness of 500Å thick is firstly coated by vaporization, and then a tri(8-hydroxyquinoline) aluminum (Alq) light emitting layer having a thickness of 400Å is coated by vaporization. After the formation of the light emitting layer, a 4Å thick LiF is coated by vaporization to form a metal salt layer, and then 2,5-bis(5,7-di-t-amyl-2-benzoxazolyl)-1,3,4-thiazole and Li-metal are simultaneously coated by vaporization on the LiF layer to form a metal-doped layer having a thickness of 300Å and a metal molar concentration of 45%. Then, a sputtering system is operated to deposit the ITO layer having a thickness of 1000 Å onto the metal-doped layer.

During the coating by vaporization, the vacuum is maintained at 6×10^{-6} torr. The anode of the device is constructed on a Si wafer integrated circuit, as highly simplifies the driving system. The resulting device has a driving voltage of 4 V and a luminance of up to 1000cd/m^2 .

The organic EL devices according to this utility model are obviously superior to the existing ones. Their cathodes are transparent while anodes can be constructed on a Si wafer integrated circuit, as highly simplifies the driving system and makes the driving voltage $\leq 4\text{V}$. Another advantage of the devices according to this utility model is that light emits out from the surface of the electron excitation electrode, *i.e.* cathode, which simplifies the production process and lowers the cost. Additionally, the structure of the organic EL device according to this utility model can also be applicable to the organic macromolecular polymer EL devices, *i.e.* the organic EL devices in which the hole transport layer and the light emitting layer both are organic macromolecular polymer materials. With respect to this kind of organic macromolecular polymer EL devices particularly, a discontinuous film-coating manner, *i.e.* some portions being coated with metals or metal salts while some portions being not coated may be used with regard to the metals and metal salts respectively doped in the metal-doped layer and the metal salt-doped layer, thus giving a discontinuous distribution of the metals or metal salts depending on the practical requirements. Thus, a potential difference between the portions doped with metals or metal salts and the portions not doped may be used to prepare templates during the fabrication. As a result, the organic EL device according to this utility model will necessarily become novel generation EL products with a strong commercial competitiveness and a promising commercial prospect.

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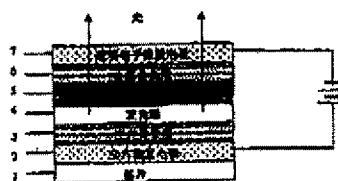
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[54] 实用新型名称 有机薄膜电致发光器件

[57] 摘要

本实用新型涉及一种有机薄膜电致发光器件,尤其涉及的是一种驱动电压 低于约 4V 的高效的透明的有机薄膜电致发光器件,其阴极由透明的电子激发 电极构成,因此该器件可从阴极的表面直接发光。该器件的构造按顺序包括空 穴激发电极、空穴传导层、发光层、金属盐掺杂层和/或金属掺杂层、透明的电 子激发电极。该器件的空穴激发电极可构造在 Si 晶片集成电路上,使得驱动大 大简便,加之不需要在阴极制模,使得工艺大为简化,显著降低了成本。该有 机薄膜电致发光器件适用于各种平板显示器,包括单色和彩色显示器,其是新 一代的具有强大市场竞争能力的 EL 换代产品。



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权 利 要 求 书

- 1、一种透明的有机薄膜电致发光器件，其特征在于：在透明的电子激发电极即阴极与发光层之间在金属掺杂层和/或金属盐掺杂层作为电子传导层。
2. 根据权利要求1的透明的有机薄膜电致发光器件，其结构按顺序包括基片、空穴激发电极、空穴传导层、发光层、金属盐掺杂层和/或金属掺杂层、透明的电子激发电极。
3. 根据权利要求1的透明的有机薄膜电致发光器件，其中掺杂的金属包括功函小于或等于4.2eV的碱金属、碱土金属、过渡金属、稀土金属；掺杂的金属盐包括功函小于或等于4.2eV的碱金属盐、碱土金属盐、过渡金属盐、稀土金属盐。
4. 根据权利要求3的透明的有机薄膜电致发光器件，其中金属盐掺杂层中掺杂的金属盐的浓度为0.1-100%(重量比)，金属掺杂层中掺杂的金属的浓度为0.1-99%(重量比)。
5. 根据权利要求4的透明的有机薄膜电致发光器件，其中金属盐掺杂层的厚度为1-3000Å，金属掺杂层的厚度为10-3000Å。
6. 根据权利要求3的透明的有机薄膜电致发光器件，其中掺杂的金属为Li、Na、K、Be、Mg、Ca、Sr、Ba、Y、La、Sm、Gd、Yb。
7. 根据权利要求3的透明的有机薄膜电致发光器件，其中掺杂的金属盐为碱金属和碱土金属氟化物、氧化物、氯化物、碘化物和碲化物。
8. 根据权利要求7的透明的有机薄膜电致发光器件，其中掺杂的金属盐为LiF、NaF、KF、RbF、CsF、MgF₂、CaF₂、SrF₂、BaF₂、Li₂O、Na₂O、K₂O、Rb₂O、Cs₂O、MgO、CaO、SrO、BaO、LiI、NaI、KI。
9. 根据权利要求6或8的透明的有机薄膜电致发光器件，其中透明的电子激发电极的材料可采用氧化铟锡(ITO)、Au、SnO₂、导电聚合物和ZnO₂。
10. 根据权利要求9的透明的有机薄膜电致发光器件，其中空穴激发电极采用溅涂沉积法来制备。
11. 根据权利要求1的透明的有机薄膜电致发光器件，其空穴激发电极构造在Si晶片集成电路上。
12. 根据权利要求6或8的透明的有机薄膜电致发光器件，其中金属盐掺杂层和金属掺杂层中的有机材料为含有孤对电子的杂原子的有机化合物，其中的杂原子为N、O、S、P。

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13. 根据权利要求 12 的透明的有机薄膜电致发光器件, 其中所述的含有孤对电子的杂原子的有机化合物为透明的, 它们的最大吸收光谱处于小于 450nm 处.

14. 根据权利要求 2 - 8、13 的透明的有机薄膜电致发光器件, 其中空穴传导层和发光层的材料为有机高分子聚合物.

15. 根据权利要求 14 的透明的有机薄膜电致发光器件, 其中金属掺杂层和金属盐掺杂层中分别掺杂的金属、金属盐的分布是不连续的.

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说明书

有机薄膜电致发光器件

本实用新型涉及一种有机薄膜电致发光器件，尤其涉及的是一种低电压驱动、阴极表面发光的多层有机薄膜电致发光器件。在此多层有机薄膜电致发光器件中，电子传导层由掺杂了金属和/或金属化合物的有机材料构成，结果其驱动电压降低；其阴极由透明的电子激发电极构成，因此该器件可从阴极的表面直接发光。该有机薄膜电致发光器件适用于各种平板显示器，包括单色和彩色显示器。

随着信息时代的飞速发展，特别是计算机的普及与推广应用，彩色显示器，特别是超薄、高分辨率的彩色平板显示器越来越受到市场的关注。高效率的便携式平板显示器，在市场上推出的已有液晶显示器（LCD），但是，液晶显示器存在以下问题：其视场角窄、响应慢、不依靠自发光，因而当置于暗环境时需要较大能耗用于背景光并有高的制作成本。

发光二极管（LED）类的显示器是作为一种换代产品。LED是一种主动发光显示技术，不存在视角差的问题，但是由于采用无机材料，受加工工艺的限制，这种显示器的制作成本也很高，驱动电压达到上百伏。

有机电致发光技术就是近年来刚刚崛起且具有极大潜在市场竞争能力的新型平板显示器。其在工艺制备、发光亮度和效率、驱动电压、分辨率、多色化和响应时间等方面具有综合优势，它具有高响应速度并且无视角问题，因此倍受关注。

有机电致发光技术已有三十多年的历史，但长期以来，有机电致发光器件存在巨大缺陷，其驱动电压 $>200V$ ，限制了其应用。

早在1965年由Gurnee等首次发表了关于有机电致发光器件的专利（US3172862；3173050）。1973年Dresner也发表了有机电致发光器件的专利（US3170167）。在这些专利中，多芳环有机化合物如蒽、四并苯、五并苯等被用作有机电致发光材料。早期的有机电致发光器件的主要结构特征为单层，有机发光层的厚度大于1mm，驱动电压在200V以上。

八十年代，美国柯达公司首次发表了超薄多层的有机电致发光器件结构，使器件的驱动电压大大降低。其器件的基本特征是以导电玻璃为衬底，先蒸度上一层空穴注入层（100nm），同时也是传导层，然后旋涂上一层电子传导层，

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同时也是发光层，最后镀上一层金属作为负极，该器件的驱动电压为 20V，亮度为 5cd/m^2 。之后，柯达公司又采用芳香多胺作为空穴传输材料，使器件的性能大大提高，亮度达到 340cd/m^2 。

之后，人们相继合成出了一系列电致发光材料。特别是近十年来由于材料及器件工艺的不断更新，使有机电致发光技术已达到或接近实用化阶段。

目前的有机电致发光器件一般是多层的复合结构，包括透明的铟-锡-氧化物 (ITO) 阳极、空穴传导层、发光层、电子传导层和不透明的金属阴极 (Al、Mg:Ag 合金或 Al:Li 合金)。空穴传导层具有将阳极注入的空穴输送至发光层的作用，电子传导层具有将阴极注入的电子输送至发光层的作用。当空穴传导层被插入发光层和阳极之间时，更多的空穴在低电场中被注入发光层中，其与从电子传导层注入发光层的电子在发光层相遇并形成激子，并最终导致发光。但目前的有机电致发光器件大多是在正常的发光亮度下驱动电压为 10V，能耗大、驱动系统复杂，而且其要在阴极制模，工艺相当复杂，对制备工艺的要求也很苛刻。

现有的有机电致发光器件的驱动电压难以进一步降低的原因是阴极与发光层间有一定能级差，载流子不易从阴极注入含有有机染料分子的发光层中，因此增强载流子注入作用被认为是改善有机电致发光器件的重要因素之一。为了降低阴极的功函，减少电子注入的势能垒，使之与电子传递层的 LUMO (最低轨道能级) 水平相当，人们增进行了大量研究，已知 Mg:Ag 或 Al:Li 合金是用于此目的的最理想的阴极材料之一，但功函低的金属对环境的稳定性差，尤其是潮湿的环境非常敏感，这使得其制备工艺变得复杂，导致成本增加，而当其暴露在空气中时会被腐蚀，因此需要对该器件进行封装处理。

另外，通常的有机电致发光器件是构造在一透明的基片例如玻璃基片上，由器件发出的光透过它来显示，由于该器件的上层即阴极是不透明的，因而只能从空穴激发电极来显示，这造成了制备工艺的复杂。尤其是当采用 Si 晶片作为基片时，由器件发出的光就被挡住，这也使得器件在材料的选择上受到限制。因此需要激发电子的电极被制成是透光的，这样有机电致发光器件发出的光就可通过此层来显示。这种结构通常被称为表面发光的有机电致发光器件 (EL)。

人们也尝试了通过选择电子传导层材料来降低与发光层之间的能级差，但现有的有机电子传输材料不能同时满足以下条件：1) 良好的导电性能；2) 优良的成膜性；3) 对制备工艺过程中的光、电、热有良好的稳定性；4) 透明。



本实用新型就是为了解决现有有机电致发光器件存在的问题，提供一种不需要使用活性金属作为阴极的高效稳定的有机电致发光器件。

本实用新型的另一目的是提供一种阳极构造在不透明的硅晶片集成电路上的有机电致发光器件。

更具体地讲，本实用新型的目的是提供了一种新型结构的驱动简便的高发射透明的有机薄膜电致发光器件，其驱动电压只有现有结构器件的驱动电压的一半。

本实用新型的另一目的是提供一种具有透明的电子激发层的高效有机电致发光显示器件。该电子激发层由透明的电子激发电极构成，这样，电致发光显示器可以从电子激发电极的表面显示，改变了以往的有机电致发光显示器因只能从空穴激发电极显示而引起的复杂制造工艺。

本实用新型的另一目的是减小电子激发电极将电子激发进入发光层的能级差，通过在电子激发电极及发光层之中加入含有金属掺杂和/或金属盐掺杂的电子传导层，从而达到降低驱动电压的效果。

本实用新型采用的掺杂于透明的电子传导有机化合物中的金属或金属盐是作为富电子掺杂，无论采用任何电子激发电极，电极与有机化合物层之间的能级差都可以消除，由此降低驱动压。

为了达到上述目的，本实用新型设计的是一种多层复合结构的有机电致发光器件，其在透明的电子激发电极即阴极与发光层之间加入了金属掺杂层和金属盐掺杂层作为电子传导层。该器件的结构按顺序包括：器件基片、空穴激发电极、空穴传导层、发光层、金属盐掺杂层和/或金属掺杂层、透明的电子激发电极。

本实用新型的有机电致发光器件的空穴激发电极可构造在 Si 晶片集成电路上和透明的玻璃基片上。

以下结合附图详细说明本实用新型。

附图 1 是本实用新型的有机电致发光显示器件结构示意图。

本实用新型提供的是一种多层复合结构的有机电致发光器件，其器件的结构构造特征在于：(1)为器件基片，(2)空穴激发电极，如铟-锡-氧化物 (ITO) 电极，(3)为空穴传导层，(4)为发光层，(5)为掺杂金属盐的电子传导层，(6)为掺杂金属的电子传导层，(7)是透明的电子激发电极，其可以是透明的 ITO 电极。

除了上述的层压结构外，本实用新型的有机电致发光器件还可包括其他的



层压结构例如空穴激发电极/空穴传导层/发光层/掺杂金属盐的电子传导层/透明的电子激发电极,空穴激发电极/空穴传导层/发光层/掺杂金属的电子传导层/透明的电子激发电极。值得注意的是,本实用新型可具有任何层压结构,只要其中含有掺杂金属或金属盐的电子传导层和透明的电子激发电极。

对于本实用新型的有机电致发光显示器,电子和空穴分别从阴极和阳极激发注入,分别在空穴传导层和电子传导层中传输,在两层的界面附近区域电子和空穴复合,并产生激子,激子通过辐射跃迁回到基态,由此发出光。电子从阴极激发到电绝缘的有机化合物层中是基于在阴极表面的电子传导层中的有机化合物的还原,产生游离阴离子态。对于本实用新型,掺杂的金属或金属盐预先被掺杂在接触阴极的电子传导有机化合物层中,它们起到还原有机化合物的作用,由此从阴极激发注入电子过程中产生的能级差被降低。由于掺杂金属或金属盐的层含有已被还原的分子(即已接受电子和含有电子的分子),注入电子的能级较小,由此降低了驱动电压。

本实用新型的器件结构中的基片是单晶半导体基片,其选自Si、Ge、GaAs、GaP、GaN、GaSb、InAs、InP、InSb或 $Al_xGa_{1-x}As$,其中x是0-1。该基片可以是不掺杂的、略掺杂或多掺杂的,并且其可以是裸露的或覆盖上一层不导电材料,例如氧化硅或氮化硅。在实际应用中,一部分半导体材料可制成器件的基片,而其余的半导体晶片可加工成驱动器、开关或其他电路。

在本实用新型的器件结构中,掺杂金属的电子传导层(6)中的掺杂金属不限于特定的一种,只要其能还原有机化合物,包括碱金属例如Li、碱土金属例如Mg、过渡金属包括稀土金属,其功函小于或等于4.2eV。这种掺杂的金属的典型实例包括Li、Na、K、Be、Mg、Ca、Sr、Ba、Y、La、Sm、Gd、Yb。金属的掺杂浓度为0.1-99%(重量比),厚度可以为10-3000Å。

掺杂金属盐的电子传导层(5)中的掺杂金属盐包括碱金属盐、碱土金属盐、过渡金属盐、稀土金属盐,其功函小于或等于4.2eV。用于本实用新型的有机电致发光器件中的掺杂的金属盐必须具有低的吸电子或强的偶极特性,这些是可能被选择的材料的关键特征。除了碱金属和碱土金属氟化物和氧化物外,其他可选择材料包括它们的混合物、氯化物、碘化物和碲化物。具体的实例包括LiF、NaF、KF、RbF、CsF、 MgF_2 、 CaF_2 、 SrF_2 、 BaF_2 、 Li_2O 、 Na_2O 、 K_2O 、 Rb_2O 、 Cs_2O 、 MgO 、 CaO 、 SrO 、 BaO 、LiI、NaI、KI等。金属盐的掺杂浓度为0.1-100%(重量比),厚度可以为1-3000Å。

若金属掺杂的浓度低于0.1%,则仅有很小的掺杂效果,因为被还原的有

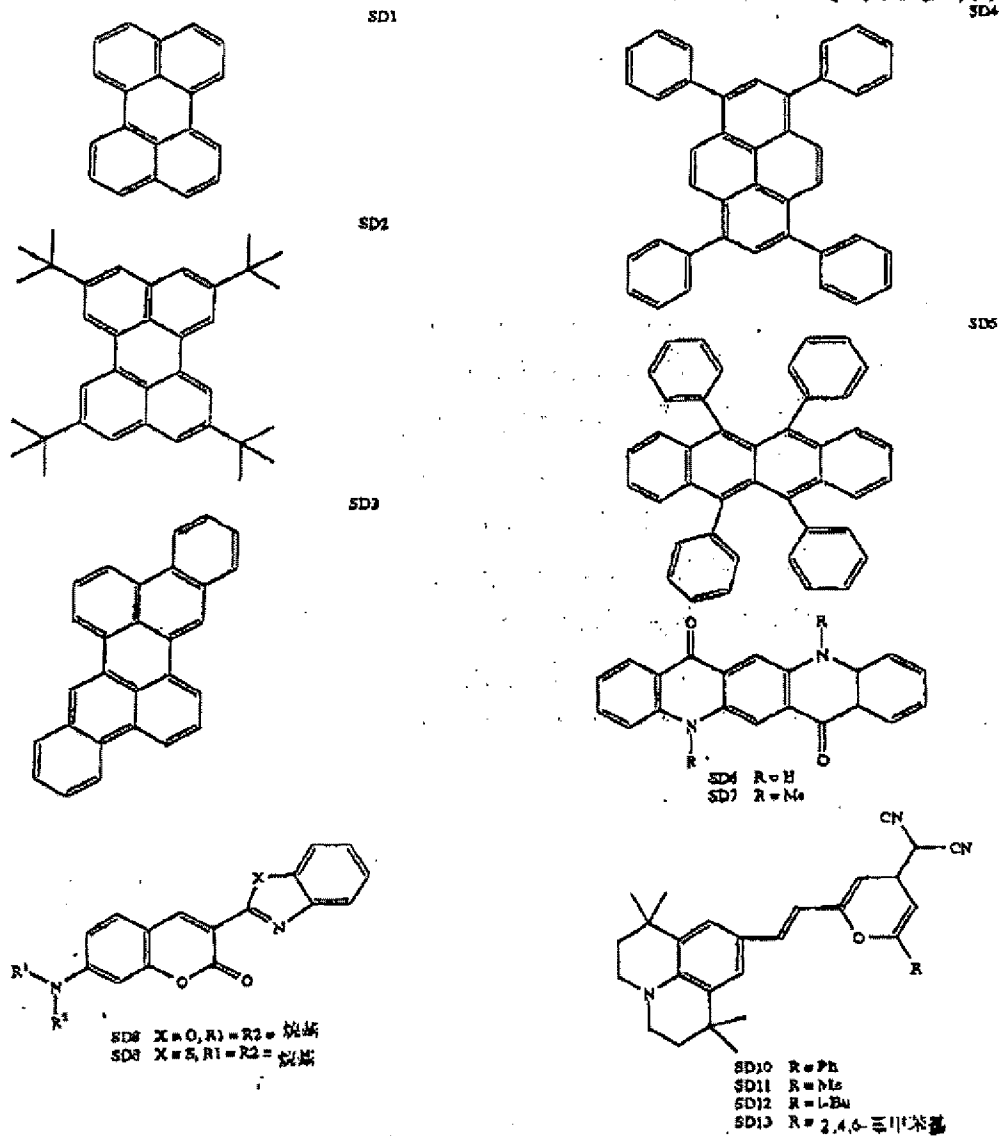
或不透明的。

用于空穴传导层的材料是采用能接受阳极的空穴和传导它们的材料，不限于一种，其可以是本领域公知的任何空穴传导材料，包括但不限于：在 JP-A-6-25659、6-203963、6-215874、7-145116、7-224012、7-157473、8-48656、7-126226、7-188130、8-40996、8-40997、7-126225、7-1011911 和 7-97355 中公开的芳胺类化合物，其具体实例包括 N,N,N',N'-四苯基-4,4'-二氨基联苯、N,N'-二苯基-N,N'-二(3-甲基苯基)-4,4'-二氨基联苯、2,2-二(4-二对甲苯基氨基苯基)丙烷、N,N,N',N'-四对甲苯基-4,4'-二氨基联苯、二(4-二对甲苯基氨基苯基)苯基甲烷、N,N'-二苯基-N,N'-二(4-甲氧基苯基)-4,4'-二氨基联苯、N,N,N',N'-四苯基-4,4'-二氨基二苯基醚、4-N,N-二苯基氨基-(2-二苯基乙烯基)苯、1,1-二(4-二对三氨基苯基)环己烷、1,1-二(4-二对三氨基苯基)-4-苯基环己烷、二(4-二甲基氨基-2-甲基苯基)苯基甲烷、N,N,N'-三(对甲苯基)胺、4-(二对甲苯基氨基)-4'-[4-(二对甲苯基)氨基]苯乙炔基]芪、N,N,N',N'-四苯基-4,4'-二氨基联苯-N-苯基吡啶、4,4'-二[N-(1-萘基)-N-苯基氨基]对三联苯、4,4'-二[N-(2-萘基)-N-苯基氨基]萘、4,4'-二[N-(3-乙酰萘次甲基)-N-苯基氨基]萘、4,4'-二[N-(9-蒽基)-N-苯基氨基]联苯、4,4'-二[N-(1-蒽基)-N-苯基氨基]对三联苯、4,4'-二[N-(2-菲基)-N-苯基氨基]联苯、4,4'-二[N-(8-蒽基)-N-苯基氨基]联苯、4,4'-二[N-(2-蒽基)-N-苯基氨基]联苯、4,4'-二[N-(1-蒽基)-N-苯基氨基]联苯、2,6-二(二-对甲苯基氨基)萘、2,6-二[二(1-萘基)氨基]萘、2,6-二[N-(1-萘基)-N-(2-萘基)氨基]萘、4,4'-二[N,N-二(2-萘基)氨基]三联苯、4,4'-二[N-苯基-N-[4-(1-萘基)苯基]氨基]联苯、4,4'-二[N-苯基-N-(2-蒽基)氨基]联苯、2,6-二

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[N,N-二(2-萘基)氨基]蒽、4,4'-二(N,N-二对甲苯基氨基)三联苯、二(N-1-萘基)(N-2-萘基)胺。空穴传导层的厚度为：300 - 5000Å。

用于发光层的材料可以是本领域公知的用于有机电致发光器件中的任何有机发光材料，可采用在薄膜状态下具有高荧光或磷光效率的有机材料，例如ALQ。也可以采用客体材料与这些高荧光或磷光效率的有机材料相掺杂形成的混合发光材料，所述的客体材料包括但不限于以下通式的化合物：



发光层的厚度为：50 - 5000Å。

用于本实用新型的有机电致发光器件中的金属、金属盐掺杂层的有机材料不限于特定的一种，它们为含有孤对电子的杂原子的有机化合物，其中的杂原子为N、O、S、P。所述的含有孤对电子的杂原子的有机化合物为透明的，

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它们的最大吸收光谱处于小于 450nm 处。适合的有机化合物的实例包括多环化合物例如对三联苯、四联苯以及其衍生物、缩合的多环烃化合物例如萘、并四苯、苊、蒽、蒽、二苯基蒽、菲以及其衍生物、缩合的杂环化合物例如菲咯啉、红菲绕啉、菲啉、吡啉、喹啉、喹喔啉、吩嗪等以及其衍生物、和二苯基丁二烯、四苯基丁二烯、噁二唑、醛连氮、二苯并噁啉、联苯乙烯、吡嗪、环戊二烯、8-羟基喹啉、氨基喹啉、亚胺、二苯乙烯、乙烯基蒽、二氨基吡啶、吡喃、硫代吡喃、聚甲炔、卟花青、喹吖啶、红荧烯以及其衍生物。除了上述的有机化合物外，在 JP - A - 63 - 295695, 8 - 22557, 8 - 81472, 5 - 9470 和 5 - 17764 中公开的金属螯合化合物也适合。在这些金属螯合化合物中，适合的是用 8-羟基喹啉以及其衍生物作为配位体的金属螯合物，具体的配位体的例子为三(8-羟基喹啉)铝、二(8-羟基喹啉)镁、二[苯并-8-羟基喹啉]锌、二(2-甲基-8-羟基喹啉)铝、三(8-羟基喹啉)铜、三(5-甲基-8-羟基喹啉)铝、8-羟基喹啉锂、三(5-氯-8-羟基喹啉)镱、二(5-氯-8-羟基喹啉)钙。其他适合的材料是二芳基丁二烯和苊，例如在 US4356429 中公开的那些，以及 US4539507 中公开的作为荧光增白剂的材料，还可使用《合成染料化学》第 5 卷，1971，第 618 - 637 中所列的荧光增白剂。特别是 2,5-双(5,7-二叔戊基-2-苯并噁唑基)-1,3,4-噻唑。

以下描述本实用新型设计的有机电致发光器件的制备方法：

- (1) 选 1 条光刻为条形电极的 ITO 透明导电玻璃电极，线条密度为 3 - 4/mm。
- (2) 将具有空穴传导性质的空穴传导材料真空蒸镀到 ITO 透明导电玻璃电极上。
- (3) 接着在空穴传导层上再蒸镀一层发光材料，形成发光层。
- (4) 在形成发光层后，在控制真空的条件下，将电子传导层材料分别与金属、金属盐一同蒸镀到发光层上，使得掺杂的金属或金属盐达到本实用新型所述的浓度范围，形成金属掺杂层和/或金属盐掺杂层，其总厚度为 1 - 3000Å。
- (5) 使用溅镀系统在金属掺杂层和/或金属盐掺杂层上沉积 ITO 层，其厚度在 50 - 5000Å 范围。

以下通过实例进一步说明本实用新型设计的有机电致发光器件：

选 1 条光刻为条形电极的 ITO 透明导电玻璃电极，线条密度为 3 - 4/mm，在该镀有 ITO 的玻璃基片上先蒸镀一层 TPD 空穴传导层，厚度为 500Å，然后蒸镀一层三(8-羟基喹啉)铝 (Alq) 发光层，厚度为 400Å。在形成发光层后，蒸镀 4Å LiF，形成金属盐层，然后将 2,5-双(5,7-二叔戊基-2-苯并噁唑基) -



1,3,4-噻唑与金属Li一同蒸镀到LiF层上,形成金属掺杂层,其中金属掺杂层中的金属摩尔浓度为45%,该层的厚度为300Å。然后操作溅镀系统,在金属掺杂层上沉积ITO层,为厚度为1000Å。在蒸镀过程中,保持 6×10^{-6} 托。将该器件的阳极构造在Si晶片集成电路上,这使得驱动系统大大简化。该器件的驱动电压为4伏,亮度可达到1000cd/m²。

本实用新型设计的有机电致发光器件明显优于现有的有机电致发光器件,其阴极为透明,其阳极可构造在Si晶片集成电路上,这大大简化的驱动系统,驱动电压达到≤约4伏。该器件另外的优点是其可从电子激发电极,即阴极表面显示,这使得其制备工艺简化,降低了成本。此外,本实用新型的有机电致发光器件的结构同样适用于有机高分子聚合物电致发光器件,即空穴传导层和发光层为有机高分子聚合物材料的电致发光器件,金属和/或金属盐掺杂层可作为所述有机高分子电致发光器件的电子传导层。特别是对于这种有机高分子电致发光器件,金属和金属盐掺杂层中分别掺杂的金属和金属盐可采取不连续镀膜方式,即某些部位镀膜上金属、金属盐,某些部位不镀膜金属、金属盐,使它们呈不连续的分布,这可根据实际的要求而定,这样掺杂了金属、金属盐的部位与没有掺杂金属、金属盐的部位由于存在电位差,则在制备工艺中,可利用该电位差来制模板。因此,本实用新型设计的有机电致发光器件必将成为新一代的具有强大市场竞争能力的EL换代产品并具有广阔的市场化前景。

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说明书附图

